

Early Journal Content on JSTOR, Free to Anyone in the World

This article is one of nearly 500,000 scholarly works digitized and made freely available to everyone in the world by JSTOR.

Known as the Early Journal Content, this set of works include research articles, news, letters, and other writings published in more than 200 of the oldest leading academic journals. The works date from the mid-seventeenth to the early twentieth centuries.

We encourage people to read and share the Early Journal Content openly and to tell others that this resource exists. People may post this content online or redistribute in any way for non-commercial purposes.

Read more about Early Journal Content at http://about.jstor.org/participate-jstor/individuals/early-journal-content.

JSTOR is a digital library of academic journals, books, and primary source objects. JSTOR helps people discover, use, and build upon a wide range of content through a powerful research and teaching platform, and preserves this content for future generations. JSTOR is part of ITHAKA, a not-for-profit organization that also includes Ithaka S+R and Portico. For more information about JSTOR, please contact support@jstor.org.

METALLIC SALTS OF AMMONO ACIDS

By Edward C. Franklin

DEPARTMENT OF CHEMISTRY, STANFORD UNIVERSITY
Presented to the Academy, January 9, 1915

The Action of Liquid-Ammonia Solutions of Ammono Acids on Metallic Amides, Imides, and Nitrides. The acid amides and imides, and the metallic derivatives of the acid amides and imides are the acids, bases, and salts respectively of an ammonia system of acids, bases, and salts.¹

Guided by the relationships implied in the above statement Franklin and Stafford were able to prepare potassium derivatives of a considerable number of acid amides by the action of potassium amide on certain acid amides in solution in liquid ammonia. That is to say, an ammono base, potassium amide, was found to react with ammono acids in liquid ammonia to form ammono salts just as the aquo base, potassium hydroxide, acts upon aquo acids in water solution to form aquo salts. Choosing, for example, benzamide and benzoic acid as representative acids of the two systems, the analogous reactions taking place respectively in liquid ammonia and water are represented by the equations:

 $C_6H_5CONH_2+KNH_2=C_6H_5CONHK+NH_3.$ $C_6H_5CONH_2+2KNH_2=C_6H_5CONK_2+2NH_3.$ $C_6H_5COOH+KOH=C_6H_5COOK+H_2O.$

The ammono acid, since it is dibasic, reacts with either one or two molecules of potassium amide to form an acid and a neutral salt.

Having thus demonstrated the possibility of preparing ammono salts of potassium by the interaction of potassium amide and acid amides in liquid ammonia solution, it was further found that ammono salts of the heavy metals may be prepared by the action of liquid ammonia solutions of ammono acids on insoluble metallic amides, imides, and nitrides—that is, by reactions which are analogous to the formation of aquo salts in water by the action of potassium hydroxide on insoluble metallic hydroxides and oxides.

In the present investigation the action of acetamide, benzenesulfonamide, and paratoluenesulfonamide on the amide of silver, on the imides of copper and lead, and on the nitride of thallium has been studied.

The method for the preparation of a typical compound may be briefly described. Pure silver amide, prepared in a two-legged reaction-tube² by thoroughly washing the precipitate resulting from the interaction of potassium amide and silver nitrate in liquid-ammonia solution, is dis-

solved in a liquid-ammonia solution of benzenesulfonamide. After adjusting the concentration of the solution and cooling in a bath of liquid ammonia a crop of beautiful crystals of the composition represented by the formula, $C_6H_5SO_2NHAg.2NH_3$, separates from the solution. On standing in a vacuum at 20° the salt loses one molecule of ammonia of crystallization. Heated at 200° it loses the second molecule.

The action of the acid on the base is shown by the equation:

$$C_6H_5SO_2NH_2 + AgNH_2 = C_6H_5SO_2NHAg + NH_3.$$

In a similar way the following salts have been obtained:

Thallous ammonobenzenesulfonate, $C_6H_5SO_2NHTl$, $C_6H_5SO_2NHTl \cdot NH_3$, and $\cdot 2NH_3$. Cuprous ammonobenzenesulfonate, $C_6H_6SO_2NHCu$ and $C_6H_6SO_2NHCu \cdot 2NH_3$. Thallous ammonoparatoluenesulfonate, $CH_3C_6H_4SO_2NHTl$, and $CH_3C_6H_4SO_2NHTl \cdot 2NH_3$. Cuprous ammonoparatoluenesulfonate, $CH_3C_6H_4SO_2NHCu$, and $CH_3C_6H_4SO_2NHCu \cdot 2NH_3$. Silver ammonoacetate, $CH_3CONHAg$ and $CH_3CONHAg \cdot 2NH_3$. Thallous ammonoacetate, $CH_3CONHTl \cdot 2NH_3$.

The Action of Liquid-Ammonia Solutions of Ammono Acids on Metallic Hydroxides and Oxides. Reactions between some of the stronger ammono acids and metallic hydroxides are known to take place in water solutions. In order to ascertain whether metallic hydroxides and oxides would dissolve in liquid ammonia solutions of acid amides to form ammono salts, cupric hydroxide and silver oxide were submitted to the action of liquid-ammonia solutions of benzenesulfonamide with the result that reactions took place as represented by the equations:

$$Cu(OH)_2 + 2C_6H_5SO_2NH_2 = 2C_6H_5SO_2NHCu + 2H_2O$$

 $Ag_2O + C_6H_5SO_2NH_2 = C_6H_5SO_2NHAg + H_2O$,

Dried *in vacuo* at 20° cupric ammonobenzenesulfonate retains four molecules of ammonia of crystallization. The silver salt is identical with the silver ammonobenzenesulfonate described above.

The Action of Liquid-Ammonia Solutions of Acid Ammono Esters on Ammono Bases. Such compounds as acetanilide and other aryl and alkyl derivatives of the acid amides are acid ammono esters which by virtue of their acid properties should be capable of reacting in liquid-ammonia solutions with metallic amides to form compounds which are at the same time ammono esters and ammono salts.

Four such compounds have been prepared; namely, silver phenyl ammonoacetate, $CH_3CONAgC_6H_5$ and $CH_3CONAgC_6H_5.NH_3$, by the action of a solution of acetanilide on silver amide; thallous phenyl ammonoacetate, $CH_3CONTlC_6H_5$, by the action of acetanilide on thallous nitride; potassium benzyl ammonoacetate, $CH_3CONKCH_2C_6H_5.NH_3$,

by the interaction of benzylacetamide and potassium amide; and potassium phenetol ammonoacetate, CH₃CONKC₆H₄OC₂H₅, by the interaction of phenetolacetamide and potassium amide.

The nature of these reactions will be clear from the equation,

$$(C_6H_5)(CH_3CO)NH + AgNH_2 = (C_6H_5)(CH_3CO)NAg + NH_3,$$

which represents the action of acetanilide on silver amide, or in other words, the action of an acid ammono ester on an ammono base.

- ¹ Franklin, Amer. Chem. J., 47, 285 (1912).
- ² Franklin, J. Amer. Chem. Soc., 27, 820 (1905).

AMMONOBASIC IODIDES OF ALUMINIUM

By Edward C. Franklin

DEPARTMENT OF CHEMISTRY, STANFORD UNIVERSITY
Presented to the Academy, January 9, 1915

While investigating the action of potassium amide on salts of aluminium in liquid-ammonia solution it was noted that a considerable amount of potassium amide could be added to aluminium iodide solutions without the formation of a permanent precipitate. Under analogous conditions in aqueous solutions aquobasic salts are formed.

The attempt was therefore made to isolate an ammonobasic aluminium iodide from a liquid-ammonia solution of aluminium iodide to which potassium amide had been added in an amount not quite sufficient to produce a permanent precipitate. When a solution so prepared is carefully concentrated a crop of well formed crystals of a compound is obtained which, after several recrystallizations, gave analytical results sharply in accord with the formula, AlI_3 . $Al(NH_2)_3$. $6NH_3$. The equation expressing its formation is $2AlI_3 + 3KNH_2 = AlI_3$. $Al(NH_2)_3 + 3KI$.

The compound is obviously related to ammonia as the ordinary basic salts are related to water. It is therefore an ammonobasic salt.

When sufficient potassium amide is added to a liquid-ammonia solution of aluminium iodide to produce a permanent precipitate a second ammonobasic salt is formed the composition of which is represented by the formula $Al(NH_2)_3.Al(NH_2)_2I.NH_3$.